HIGH PRODUCTION VOLUME (HPV)

CHALLENGE PROGRAM

TEST PLAN

For

Methylcyclopentadienyl Manganese Tricarbonyl
(MMT®)

Prepared by
The American Chemistry Council
Petroleum Additives Panel
Health, Environmental, and Regulatory Task Group

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LIST OF MEMBER COMPANIES IN THE
HEALTH, ENVIRONMENTAL AND REGULATORY TASK GROUP

The Health, Environmental, and Regulatory Task Group (HERTG) of the American Chemistry Council Petroleum Additives Panel includes the following member companies:

Chevron Oronite Company, LLC

Crompton Corporation

Ethyl Corporation

ExxonMobil Chemical Company

Ferro Corporation

Groupe SNPE

Infineum

The Lubrizol Corporation

Rhein Chemie Corporation

Rhodia, Inc.

1.0 INTRODUCTION

In March 1999, the American Chemistry Council (formerly the Chemical Manufacturers Association) Petroleum Additives Panel Health, Environmental, and Regulatory Task Group (HERTG), and its participating member companies committed to participate in the Environmental Protection Agency (EPA) High Production Volume (HPV) Chemical Challenge Program for certain chemicals. This test plan follows up on that commitment. Specifically, this test plan sets forth how the HERTG intends to address the relevant endpoints for the following substance- Methylcyclopentadienyl Manganese Tricarbonyl (CAS No.: 12108-13-3)

In preparing this test plan the following steps were undertaken:

Step 1: A review of the literature and confidential company data was conducted on the physicochemcial properties, mammalian toxicity endpoints, and environmental fate and effects for Methylcyclopentadienyl Manganese Tricarbonyl (CAS No.: 12108-13-3) using its CAS number, CAS name, and synonyms. Searches included the following sources: MEDLINE, BIOSIS, CANCERLIT, CAPLUS, CHEMLIST, EMBASE, HSDB, RTECS, EMIC, and TOXLINE databases; the TSCATS database for relevant unpublished studies on these chemicals; and standard handbooks and databases (e.g., Sax, CRC Handbook on Chemicals, IUCLID, Merck Index, and other references) for physicochemical properties.

Step 2: The compiled data was evaluated for adequacy in accordance with the EPA guidance documentation.

2.0 GENERAL SUBSTANCE INFORMATION

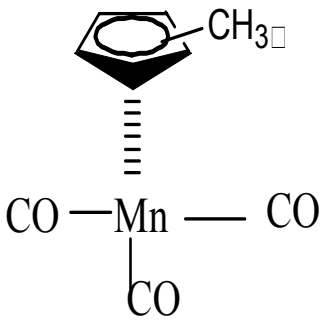
The substance that is the subject of this test plan is used as a petroleum additive in petroleum base stocks. The chemical name, CAS Registry Number, molecular weight and chemical structure for this substance are presented below.

Chemical Name: **Methylcyclopentadienyl Manganese Tricarbonyl (**MMT)

Chemical Abstract Service Registry Number: 12108-13-3

Molecular Weight: 218.1

Chemical Structure:



12108-13-3

3.0 EXPOSURE INFORMATION

Manufacture

Methylcyclopentadienyl Manganese Tricarbonyl (MMT) is manufactured at a plant that is under a toll manufacturing agreement with a member of the HERTG.

The manufacturing process entails the following. Under a nitrogen atmosphere, methylcyclopentadienyl dimer is added to a dispersion of sodium metal in diethylene glycol dimethyl ether. A constant elevated reaction temperature is maintained to yield sodium-methylcyclopentadienyl, an intermediate in the reaction process. Manganese chloride is then added to the stirred mixture containing the sodium – methylcyclopendienyl intermediate. An elevated temperature is maintained during the addition. Upon completion, the reaction gives bis(methylcyclopentadienyl)manganese, the second intermediate of the reaction process. The reaction vessel is then pressurized with carbon monoxide. The addition of carbon monoxide results in MMT which is separated from the reaction mixture via vacuum distillation.

Use

MMT is a fuel additive that boosts gasoline octane and improves combustion. MMT also helps lower tailpipe emissions of NOx and reduce refinery emissions of nitrous oxide. Both emissions are so called "green house gasses" that may be linked to global warming.

Distribution

MMT is shipped in specially designed containers that are engineered to withstand pressure, dropping and the rigors associated with transportation. At the customer's site the product is transferred from the transportation container to bulk storage tanks. The transfer is accomplished under a nitrogen atmosphere designed to reduce the potential for vapors to be released to the environment. Empty transportation containers are returned. From the storage tank, customers blend MMT into fuel using dedicated metering pumps designed to add the desired quantities. Typically, only 10 to 40 PPM of manganese is added to gasoline; thus MMT is very dilute in gasoline. Gasoline with and without MMT has the same toxicity, i.e., the MMT is such a dilute component of the fuel it presents no health issues beyond that of the gasoline itself. Gasoline

containing MMT requires no special handling and customers distribute it through normal operating procedures.

Safe product handling is promoted through on-site training sessions, videos, and manuals. A transportation driver's manual, an occupational handling manual, and medical guide detail practices and emergency procedures should an accident occur.

Workers involved in MMT manufacture are a potentially exposed population. However, monitoring at the manufacturing site has revealed no exposure issues. Other populations potentially exposed to MMT are personnel involved in the transport, off-loading and blending of MMT into fuel. The safety engineering of the transportation containers, the fact that off-loading is accomplished under a nitrogen atmosphere designed to reduce the potential for vapors to be released to the environment, and the slow metering of the additive into fuel to achieve the very dilute concentration greatly diminish the possibly of exposure. Auto mechanics and consumers fueling their vehicles are potentially another exposed population.

If exposure were to occur, the most likely routes would be skin absorption, inhalation, and contact with the eye. Protective clothing, face shields, and engineering controls that are part of the safe handling training minimize the likelihood of occupational exposures. Harmful exposure of the general population to MMT is not reasonably expected to occur due to the very dilute concentration of the additive.

4.0 PHYSICOCHEMICAL PROPERTIES

4.1 Summary of Available Data
MMT has a boiling point of 231.67 ^{o}C and a vapor pressure of 0.05 mm Hg @ 20ºC.

4.2 Data Assessment and Test Plan for Physicochemical Properties Relevant to Environmental Fate
The water solubility at 20ºC is 29 mg/L. The octanol/water partition coefficient Log Kow=3.7. MMT is a liquid and, therefore, the melting point is not applicable.

5.0 ENVIRONMENTAL FATE DATA

5.1 Biodegradability

5.1.1 Summary of Available Data
An OECD 301 D was conducted on MMT which showed that the chemical is not readily biodegradeable.
5.1.2 Data Assessment and Test Plan for Biodegradability
The available biodegradability data are adequate and reliable. No additional biodegradability tests of MMT will be conducted.

5.2 Hydrolysis

5.2.1 Summary of Available Data

No published or unpublished hydrolysis studies of MMT were located.

5.2.2 Data Assessment and Test Plan for Hydrolysis

The potential for MMT to hydrolyze will be characterized in a technical discussion.

5.3 Photodegradation

5.3.1 Summary of Available Data

Photochemical decomposition study was conducted on MMT. The half-life in mid day sunlight ~1 minute, disappearance quantum yield is 0.13

5.3.2 Data Assessment and Test Plan for Photodegradation

The available photodegradation data are adequate and reliable. No further testing will be conducted on MMT.

5.4 Fugacity Modeling

5.4.1 Summary of Available Data

There are no published or unpublished fugacity-based multimedia fate modeling data for MMT.

5.4.2 Test Plan for Fugacity

The relative distribution of MMT among environmental compartments will be evaluated using Level I Fugacity modeling.

Input data to run the EQC Level I model will require an additional computer model to estimate physical/chemical properties from a structure. The model used for this purpose will be EPIWIN, version 3.02[1], which was developed by the Syracuse Research Corporation. EPIWIN includes algorithms for estimating all physical and chemical properties needed for the EQC model.

6.0 ECOTOXICOLOGY DATA

6.1 Aquatic Ecotoxicity Testing

6.1.1 Summary of Available Data

The 48 hour EC_{50} of MMT determined in *Daphnia* is 0.83 mg/L. Reliable aquatic ecotoxicity data for fish and reliable aquatic ecotoxicity data algae are not available.

6.1.2 Data Assessment and Test Plan for Acute Aquatic Ecotoxicity

[1] Environmental Science Center- Syracuse Research Corporation- EPI for windows.

The available acute aquatic toxicity data in *Daphnia* and fish are adequate and reliable. Additional testing will be performed in algae according to OECD Test Guideline 203.

7.0 MAMMALIAN TOXICOLOGY DATA

7.1 Acute Mammalian Toxicity

7.1.1 Summary of Available Data

Several acute oral and dermal toxicity studies and an acute inhalation toxicity study are available for MMT. In these studies, the oral LD_{50} ranged from 58 to 175 mg/kg and the dermal LD_{50} ranged from 140-795 mg/kg. The 1 and 4 hour LC_{50}s in male rats were 0.247 and 0.076 mg/L, respectively.

7.1.2 Data Assessment and Test Plan for Acute Mammalian Toxicity

Adequate and reliable acute oral, dermal and inhalation toxicity tests were performed for MMT. Additional acute mammalian toxicity testing will not be conducted.

7.2. Mutagenicity

7.2.1 Summary of Mutagenicity Data

A negative *Salmonella typhimurium* point mutation assay is available for MMT. In Chinese Hamster Ovary cells, in the presence of metabolic activation, MMT induced structural chromosomal aberration. Without metabolic activation, MMT failed to induce a significant increase in chromosomal aberrations.[2] An in vivo mouse micronucleous test did not demonstrate any chromosome aberration effects.

7.2.2 Data Assessment and Test Plan for Mutagenicity Toxicity

An adequate and reliable *Salmonella typhimurium* point mutation assay and chromosomal aberration test are available for MMT. No further testing will be conducted.

7.3 Repeated-dose, Reproductive and Developmental Toxicity

7.3.1 Summary of Repeated-Dose Toxicity, Reproductive and Developmental Toxicity Data

A 14-week repeat exposure inhalation toxicity study in male and female rats and mice and in male primates and a developmental toxicity study in rats are available on MMT. The no observed adverse effect level in the 14-week inhalation study was 0.3 ug/L. MMT did not exhibit developmental toxicity at dose levels up to and including 9 mg/kg/day (gestation days 6-15).

No published or unpublished reproductive toxicity studies on MMT were located; however, the 14 week repeat exposure inhalation study conducted in rats, mice and primates included the microscopic evaluation of both male and female rat and mouse and male primate reproductive

[2] Blakey and Bayley, Environmental Molecular Mutagenesis."Induction of Chromosomal Aberrations by the Fuel Additive MMT in Chinese Hamster Ovary Cells". 1995, 25.

organs. No reproductive toxicity was observed at the high exposure level (30.2 ug/L) in any species. This study satisfies both repeat dose toxicity and reproductive toxicity for HPV purposes.

7.3.2 Data Assessment and Test Plan for Repeated-dose Toxicity

An adequate and reliable 14-week repeat exposure inhalation toxicity study on rats, mice and primates and an adequate and reliable developmental toxicity study in rats are available on MMT. The repeat exposure study meets the HPV program for both repeat dose toxicity and reproductive toxicity. No additional repeat dose, reproductive or developmental toxicity testing will be conducted.

8.0 SUMMARY

The following table summarizes the available data and proposed testing on MMT.

Table 1
Summary Table of Available Data and Proposed Testing on
Methylcyclopentadienyl Manganese Tricarbonyl

CAS No.: 12108-13-3	Study Results	Testing Proposed
Physical/Chemical Characteristics		
Melting Point	Liquid	Not applicable
Boiling Point	231.67 ^{o}C	No
Vapor Pressure	0.05 mm HG @ 20ºC	No
Water Solubility	29 mg/L	No
Partition Coefficient	3.7	No
Environmental Fate		
Biodegradation	Not readily biodegradeable	No
Hydrolysis	No Data Located	Technical Discussion
Photodegradation	Half-life in midday sunlight~1 minute	No
Fugacity	No Data Located	Yes
Ecotoxicity		
Acute Toxicity to Fish	No Data Located	Yes
Acute Toxicity to Invertebrates	Daphnia 48 Hr EC50: 0.83 mg/L	No
Acute Toxicity to Algae	No Data Located	Yes
Mammalian Toxicity		
Acute Toxicity	Oral LD50: 58-175 mg/kg (rat) Dermal LD50: 140-795 mg/kg (rabbit) Inhalation 1 Hour LC50: 0.247 mg/L (rat) Inhalation 4 Hour LC50: 0.076 mg/L (rat)	No
Repeated Dose Toxicity	14 Week Inhalation NOAEL: 0.3 ug/L (rat)	No
Developmental Toxicity	NOEL: 9 mg/kg/day (gestation days 6-15)	No
Reproductive Toxicity	14 Week Inhalation Study-Reproductive Toxicity NOEL: 30.2 ug/L	No
Genotoxicity		
Gene Mutation	Negative	No
Chromosomal Aberration	in vitro CHO without activation-positive; In vitro CHO with activation and in vivo in mouse-negative	No